

## 2. MATERIALS FOR FUEL SYSTEMS

### A. Low-Cost, High-Toughness Ceramics

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#### Objectives

- Develop high-toughness materials that are also low in cost.

#### Approach

- Develop TiC-based composites with 40–60 vol % Ni<sub>3</sub>Al to take advantage of their expansion characteristics, which are very close to those for steel.
- Conduct a development effort in collaboration with CoorsTek, Inc., and Cummins Engine on processing scale-up and engine testing.

#### Accomplishments

- Supplied a large batch of processed powder mixtures to CoorsTek for injection molding of test components.
- Sintered injection-molded components for engine testing in fuel injection systems.

#### Future Direction

- Complete work with CoorsTek (a parts supplier) to scale up the processing and to supply CoorsTek with pilot-plant-scale quantities of powder mixtures for injection molding trials.
- Supply sintered parts produced in conjunction with CoorsTek to Cummins Engine Co. for rig testing of machined components.

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### Introduction

TiC-Ni<sub>3</sub>Al composites are under development for application in diesel engines because of desirable physical and mechanical properties. For these applications, the Ni<sub>3</sub>Al volume content is on the order of 30 to 50 vol % in order to match the thermal expansion

of steel. Typically, flexural strengths greater than 1000 MPa up to 800°C and fracture toughnesses higher than 15 MPa√m are obtained for the composites. The composites are densified by liquid-phase sintering, and most of the early work used gas-atomized Ni<sub>3</sub>Al particles with fine TiC powders.

Later work was done using Ni and NiAl powders (along with the TiC) to form Ni<sub>3</sub>Al by an in-situ reaction during sintering. Over the last few years, the in-situ reaction process was developed significantly because it produced high mechanical properties and developed a fine TiC grain size. The finer grain sizes were favored because of better wear resistance.

The fabrication techniques and equipment employed in production are very similar to those for the fabrication of WC-Co hard metals, and thus the processing costs are well established. However, when the economics of producing the TiC-Ni<sub>3</sub>Al composites were examined, a significant cost was associated with the use of the NiAl precursor powder (about 55% of the total raw material cost). Because the costs of the starting raw materials can be a significant fraction of the total cost of a component, alternative materials for fabricating the cermets are of interest. Part of the reason for the high cost of the NiAl is that it is produced only as a specialty powder at the present time. The development effort is being done in collaboration with CoorsTek.

## Results

### Large-Batch Processing of TiC-Ni<sub>3</sub>Al Composites

Several large batches (>3 kg each) of a 50% TiC-Ni<sub>3</sub>Al (with 2% molybdenum) composition have been milled and blended together to produce ~13 kg of powder. Approximately 10 kg was sent to CoorsTek for injection molding testing. A large batch (>3 kg) was also produced that used a cheaper NiAl powder from the same manufacturer that was coarser than that previously used. Much of the earlier work used powder that had particle sizes  $\leq 20$   $\mu\text{m}$ . The batch produced recently used NiAl powder with particle sizes  $\leq 150$   $\mu\text{m}$  (-100 mesh).

The sintering furnace used for processing studies was out of service for many months because of a bad controller and was repaired during the last quarter of the fiscal year. However, sintering runs were completed on injection-molded test components from CoorsTek. These parts were sintered and sent

to Coors-Tek and Cummins Engine Company for final component finishing and engine testing.

### Alternate Precursors for Ni<sub>3</sub>Al Formation

All previous work used a combination of Ni and NiAl for an in-situ reaction to form the Ni<sub>3</sub>Al. Because the costs of the starting raw materials can be a significant fraction of the total cost of a component, alternative materials for fabricating the cermets are of interest. Several new batches were milled and pressed into discs and billets. The compositions are described in Table 1.

As shown, several different compositions are being examined. The new batch of Al-30 Ni from the catalyst manufacturer will determine if these materials can be made without the impurities, as observed previously. Earlier work demonstrated that these precursors produced high-density parts but had low strengths because of impurity contamination. One of the other samples will re-examine the use of pre-alloyed Ni<sub>3</sub>Al (made by gas atomization). Earlier work at high TiC contents (70–90 vol %) showed these Ni<sub>3</sub>Al powders produced non-homogeneous microstructures with large “pools” of Ni<sub>3</sub>Al surrounded by the finer TiC grains. However, with the TiC content of interest now at 50 vol %, the presence of the Ni<sub>3</sub>Al pools may not be significant to the performance of the cermets. Samples were also fabricated using a commercial Hastelloy X powder. This is a Ni-Cr-Fe-Mo alloy with good oxidation and corrosion resistance.

An attempt was made to make a pre-reacted Al-Ni precursor that could be milled to fine sizes during the normal processing of the cermets (Sample DC-3-10). Thermodynamic calculations indicated that the lowest heat of formation per gram was associated with making Al<sub>3</sub>Ni. Appropriate amounts of aluminum and nickel were dry-milled and then fired (at a slow heating rate) to 700°C, which is sufficient to melt the aluminum. The resulting reacted product was very hard and non-friable. Consequently, this route to producing an Al-Ni precursor did not appear to be one with significant potential.

**Table 1.** Summary of TiC-Ni<sub>3</sub>Al compositions fabricated

Batch no.	TiC content (vol %)	Ni <sub>3</sub> Al source
DC-3-7	50	NiAl + Ni (milling done with larger WC media)
DC-3-8	50	Al-30 Ni Catalyst (new batch from manufacturer)
DC-3-9	50	Pre-alloyed Ni <sub>3</sub> Al (-325 mesh)
DC-3-10	50	Reacted Al <sub>3</sub> Ni
DC-3-11	50	Hastelloy X

## **Conclusions**

Pilot scale batches of TiC-Ni<sub>3</sub>Al composite mixtures were produced. In collaboration with Coors-Tek, injection-molded components were fabricated and sintered to high density. The parts will be used for engine testing by Cummins Engine Company.

## **Publications/Presentations**

T. N. Tiegs, F. C. Montgomery, and D. A. Menchhofer, "Effect of NiAl Precursor Type on Fabrication and Properties of Ni<sub>3</sub>Al-Bonded Carbide Composites," presented at the American Ceramic Society Conference on Ceramics and Composites, Cocoa Beach, FL, Jan. 25–28, 2004.

T. N. Tiegs, F. C. Montgomery, and P. A. Menchhofer, "Effect of Ni-Al Precursor Type on Fabrication and Properties of TiC-Ni<sub>3</sub>Al Composites," to be published in *Ceram. Eng. Sci. Proc.*



## B. Low-Cost Manufacturing Processes for Ceramic and Cermet Diesel Engine Components

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*Contractor: Oak Ridge National Laboratory, Oak Ridge, Tennessee*

*Prime Contract No.: DE-AC05-00OR22725*

*Subcontractor: Southern Illinois University, Carbondale, Illinois*

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### Objective

- Investigate higher continuous sintering rates as a more cost-effective manufacturing process for ceramic and cermet diesel engine components.

### Approach

- Process cermet compositions containing titanium carbide (TiC) and nickel aluminide intermetallic matrix phase into cylindrical shapes by standard dry pressing techniques.
- Sinter the cermets by continuous sintering at much higher sintering rates than previously investigated.
- Measure physical properties and compared them with previously processed materials.

### Accomplishments

- Modified the continuous furnace at Southern Illinois University–Carbondale (SIUC) to allow for the investigation of higher sintering rates, which appear to produce more uniform microstructures in nickel aluminide bonded TiC cermets. Higher sintering rates could lead to improved economics of production, while more uniform microstructures give inherently more uniform properties and performance.
- Continued interaction with Oak Ridge National Laboratory (ORNL) and CoorsTek to promote commercialization of cermet diesel engine components.

### Future Direction

- The past year was the final year of funding for this project. However, exploration of the use of higher sintering rates for other potential cermet formulations should be continued.

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### Introduction

All manufactured parts can potentially benefit from improved manufacturing processes and the incorporation of advanced materials. Injection molding has been previously shown to be a very cost-

effective method for producing precision parts with minimal labor cost, and continuous sintering has been proven industrially to provide an economic advantage for sintering many advanced ceramics. More recently, continuous sintering has been used as

a means of rapid sintering of cermets composed of TiC in an intermetallic matrix.

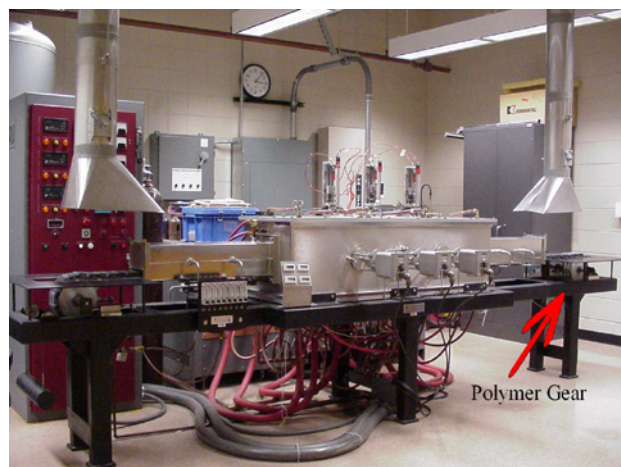
To reduce costs, it is essential to minimize material waste while maximizing the yield of finished parts that are within specifications. A potential means of maximizing the furnace yield of parts that are in-specification while minimizing material losses due to furnace-related problems, thereby reducing part cost, is the use of continuous sintering. The continuous furnace at SIUC has been used to sinter a wide range of pre-alloyed intermetallic-TiC formulations and similar formulations where the intermetallic is formed by reaction sintering of the individual elements. Based on this work, the most promising intermetallics contained 30–50 vol % of NiAl, NiC, or NiCrFe added to a fine-grained commercial TiC. These formulations were found to have high strength, hardness, toughness, and corrosion resistance. In addition, their thermal expansion can be engineered to be very close to that of cast iron and steel, which will reduce thermal expansion mismatch in several key diesel engine applications.

The present work was focused on modifying the continuous furnace to allow for higher transport rates through the furnace without causing damage to the furnace structure. Once modified, cermets were sintered at much higher sintering rates than previously investigated. Also, interactions were continued with ORNL and CoorsTek to promote commercialization of these cermets for diesel engine components.

## **Approach**

### **Continuous Furnace Modification**

The continuous furnace was constructed using an ultra-high molecular weight polyethylene (UHMW-PE) gear on the exit end of the furnace. This was done to give some flexibility to the ceramic link belt and to avoid stresses that might cause the ceramic pins in the belt to fracture. Attempting to run the continuous furnace at high transport speeds, in excess of about 1.5 in./min (4.31 cm/min), when the furnace temperature exceeded 1400°C, caused overheating of the UHMW-PE gear. It was believed that running for extended periods of time at these rates or higher would eventually cause damage to the ceramic link belt. Figure 1 shows the continuous furnace and Figure 2 shows the original



**Figure 1.** Continuous furnace at SIUC showing location of original polymer gear.

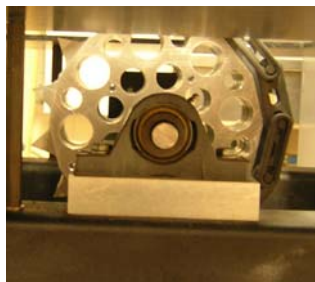


**Figure 2.** Original ultra-high molecular weight polyethylene gear.

polymer gear. To eliminate this problem, an aluminum alloy, 6061-T6, gear was designed and machined at SIUC. Figure 3 shows the new aluminum alloy gear installed on the continuous furnace exit drive. As seen, several holes were machined in the gear to improve heat transfer, which allows the gear to run cooler.

### **Investigation of High Heating Rates**

Previous continuous sintering of cermets at SIUC was accomplished at sintering rates less than or equal to 125°C/min. This task investigated the use of continuous sintering as a means of obtaining high heating rates (>125°C/min) in the liquid-phase sintering of Ni<sub>3</sub>Al-TiC cermets. Since the continuous furnace uses a ceramic belt to transport the load through the hot zone, the heating rate is dependent on the belt speed. The modification of the furnace allowed the investigation of much higher heating rates than previously investigated. The cermets investigated are sintered by liquid-phase sintering; therefore, employing high heating rates could enhance particle rearrangement and solution precipita-



**Figure 3.** Aluminum alloy gear installed.

tion during the formation of the liquid. In the  $\text{Ni}_3\text{Al-TiC}$  system, TiC is known to be soluble in the intermetallic, with about 4% Ti remaining in solution in the  $\text{Ni}_3\text{Al}$ . It was hoped that the high heating rates would lead to enhanced solution and precipitation of the TiC, thereby producing finer TiC in the microstructure.  $\text{Ni}_3\text{Al-TiC}$  cermet containing 50 vol % intermetallic were sintered in flowing argon at  $1450^\circ\text{C}$ , using four different belt speeds that corresponded to heating rates of 125, 250, 500 and  $750^\circ\text{C/min}$ . Soak time at peak temperature was held constant at 30 min. Following sintering, density and microhardness were determined and the microstructure investigated by scanning electron microscopy (SEM).

### **Industrial Collaboration**

Collaboration between SIUC, ORNL, and CoorsTek has continued since the start of this project. Cermet processed by low-pressure injection molding and continuous sintering were submitted to ORNL for wear testing, and materials have been submitted to CoorsTek for evaluation. During this project period, CoorsTek submitted materials to SIUC for sintering and evaluation.

### **Results**

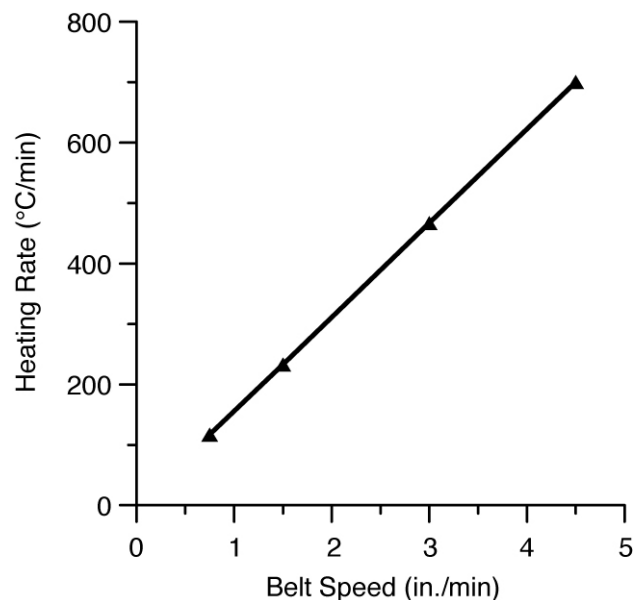
#### **Furnace Modification**

The furnace was modified as planned by the addition of the aluminum alloy gear, as shown in Figure 3. This modification allowed the belt speed to be increased from 0.75 to 4.5 in./min (1.9 to 11.43 cm/min), which is equivalent to 125 and  $750^\circ\text{C/min}$ , respectively. This is assuming a maximum hot-zone temperature of  $1450^\circ\text{C}$  and all three zones being at temperature. Obviously, higher hot-zone temperatures would lead to higher heating rates. This is significant in that traditional production furnaces usually do not exceed heating rates of

over  $50^\circ\text{C/min}$ , and usually operate at much lower temperatures.

### **Investigation of High-Heating Rates**

As reported, four different heating rates were investigated. Figure 4 shows the equivalent heating rate as a function of belt speed.

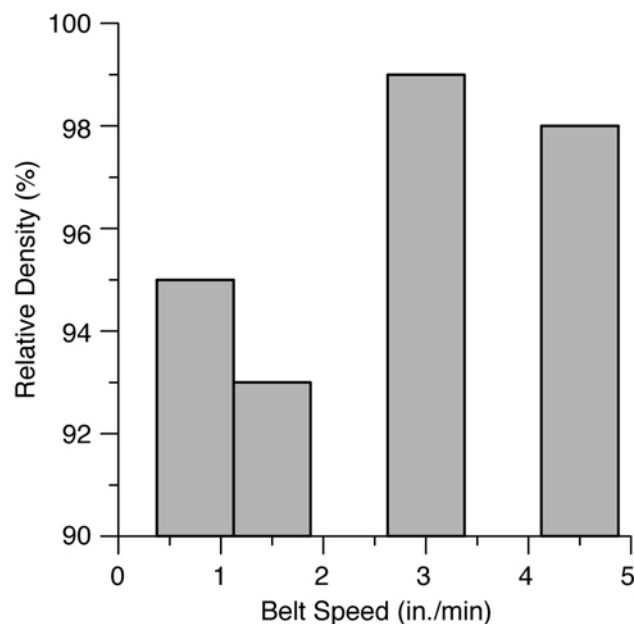


**Figure 4.** Heating rate as a function of belt speed.

The resulting density results are shown in Figure 5. The relative density achieved was higher at the higher heating rates, with the belt speed of 3.0 in./min (7.62 cm/min) or heating rate of  $500^\circ\text{C/min}$  giving the highest density results.

As seen in Figure 6, the lower sintering rates produced microstructures in which the intermetallic appears as large pools. The bright phase is the intermetallic, and the dark phase is the TiC or, in some cases, porosity. These intermetallic pools were found to be reduced in size at the higher heating rates. At the highest heating rate,  $750^\circ\text{C/min}$ , the pools appear to have been eliminated. In addition, there appears to be more rounding of the TiC particles at the higher heating rates.

Some potential advantages of the higher heating rates appear to be obvious. The use of the continuous furnace has been found previously to offer a reduction of as much as 50% in the sintering costs for advanced ceramics. A similar saving could be anticipated for cermet if the properties obtained are acceptable. The higher heating rates obviously



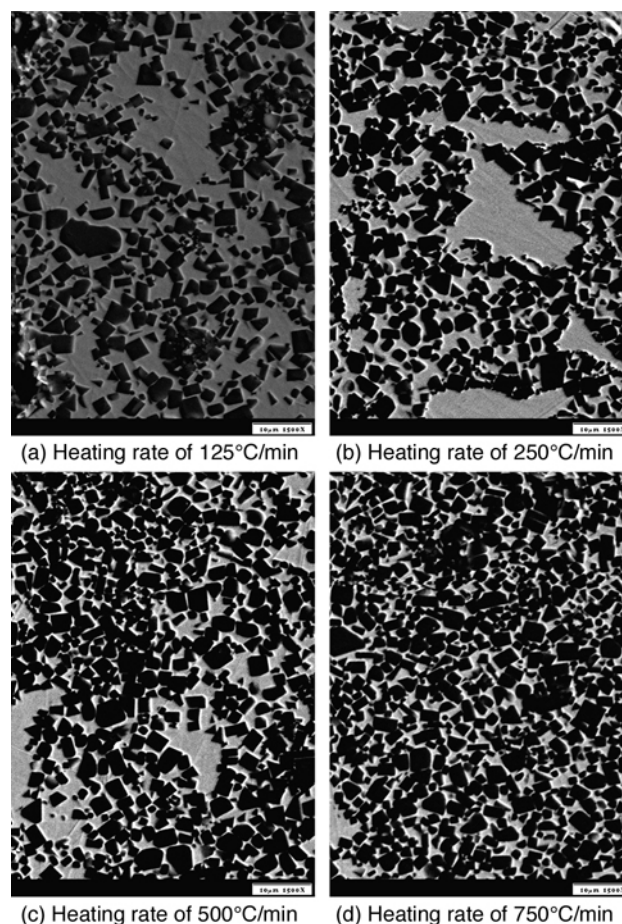
**Figure 5.** Relative density as a function of belt speed.

would allow for the production of more parts per shift, which would further reduce the overall manufacturing cost. An additional advantage of the high heating rate appears to be more uniform microstructures, which should in turn produce more uniform properties for the cermets.

### **Industrial Collaboration**

SIUC, ORNL, CoorsTek, and Cummins have been involved in a confidential collaboration, and all data related to this project have been the responsibility of the individual contributors. During this reporting period, SIUC received four test bars from CoorsTek for continuous sintering and evaluation. None of the test bars was sintered without warping, and the densities obtained were well below the benchmark set by CoorsTek.

The results of wear testing at ORNL have been very favorable for many of the cermets investigated. The hardness, toughness, and strength of the cermets investigated are responsible for the very high wear resistance. The effects of wear resistance of the intermetallic and of particle size of the TiC in the cermet are not very well understood. Several of the simple cylindrical shapes produced at SIUC were previously submitted to Peter Blau at ORNL for sliding wear evaluation. The results continue to be encouraging.



**Figure 6.** SEM microstructures for the four heating rates investigated.

### **Conclusions**

The continuous furnace was modified to allow for higher heating rates.  $\text{Ni}_3\text{Al-TiC}$  cermets containing 50 vol % intermetallic were sintered in flowing argon at 1450°C using four different belt speeds corresponding to heating rates of 125, 250, 500 and 750°C/min. Higher heating rates produced higher densities and more uniform microstructures than the lower heating rates. Higher heating rates could lead to improved production costs by increasing part throughput.

### **Presentation**

Dale E. Wittmer and Joshua W. Steffen, "Effect of High Sintering Rates on Microstructure of  $\text{Ni}_3\text{Al-TiC}$  Cermets," (poster presentation at PM2TEC 2004, Chicago, IL, June 13–17, 2004), pp. 38–43 in *Advances in Powder Metallurgy and Particulate Materials*, Part 9, 2004.



## C. Cermet Composites for Wear Applications

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*Contractor: Oak Ridge National Laboratory, Oak Ridge, Tennessee*

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*Subcontractor: Cummins, Inc., Columbus, Indiana*

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### Objectives

- Optimize injection molding binder composition and sintering cycles to achieve 99+% density. This will include determination of the shrink rate during sintering for prototype tool construction and demonstration.
- Test prototype components in an intended application on Cummins Fuel System test rigs to show the viability of the material in an application.

### Approach

- Make a prototype injection molding tool of a proposed Cummins Fuel Systems component and produce test pieces of the TiC/Ni<sub>3</sub>Al cermet to near-net shape for evaluation of shrinkage, microstructure uniformity, and density.
- Conduct abuse tests of prototypes machined from isostatically pressed rods of the TiC/Ni<sub>3</sub>Al cermet at Cummins Fuel Systems.

### Accomplishments

- Achieved a 99+% dense structure with the injection molding process. The TiC distribution within the Ni<sub>3</sub>Al matrix was uniform, and there was good wetting of the TiC particles. The shrink rate was also determined.
- Successfully tested prototypes at Cummins Fuel Systems. The components are required to withstand both sliding and impact wear. No adverse wear was observed after the testing.

### Future Direction

- Finalize the design and test the injection-molded materials on Cummins Fuel Systems test rigs.
  - Determine and/or develop a supply base for raw material constituents.
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## Introduction

Increasingly stricter diesel engine combustion emission standards and the desire of buyers for maintained or improved fuel economy require that fuel injection systems become more advanced. Higher fuel injection pressures (to aid emissions control) and more precise control of when and how much fuel is injected (for both emissions control and fuel economy) are required. New materials that exhibit excellent wear properties against steel components are needed for applications where components slide and impact against each other. One material that Cummins is interested in was developed under a DOE cooperative agreement: TiC/Ni<sub>3</sub>Al.

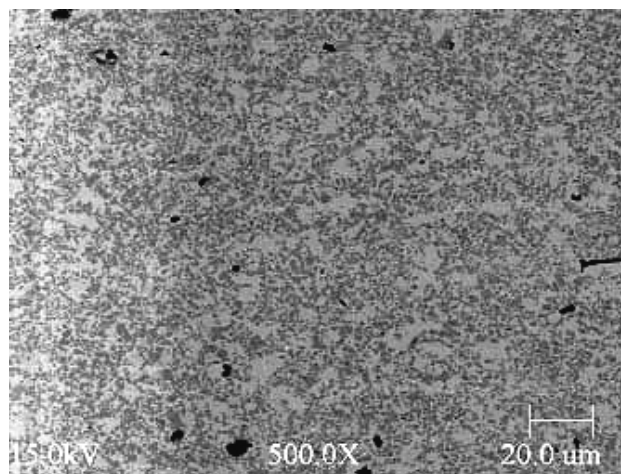
TiC/Ni<sub>3</sub>Al is a composite of TiC powder in a Ni<sub>3</sub>Al matrix that was developed in collaboration with Oak Ridge National Laboratory (ORNL) and CoorsTek. Its composition was established to match the unique properties required for Cummins Fuel Systems applications. CoorsTek and ORNL have developed the processing methods to make the material, while Cummins has been responsible for finding an application for it, testing the material in fuel system components, and evaluating its performance against that of other materials.

## Approach

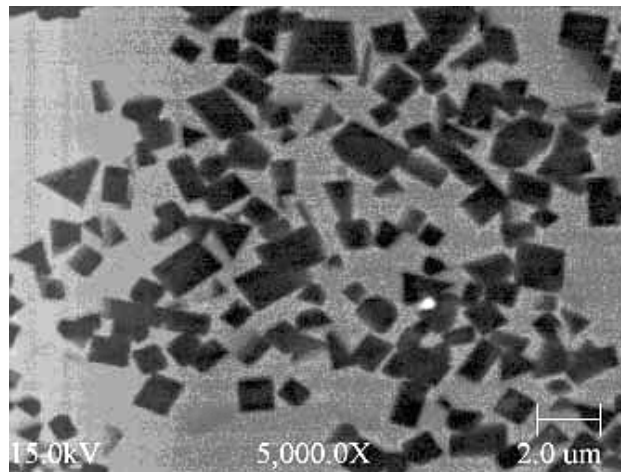
The established composition of TiC/Ni<sub>3</sub>Al cermet will be processed using the powder injection molding process to create a near-net shape component. Its microstructure, density, and shrinkage rate will be evaluated to determine the effectiveness of the manufacturing process. Coinciding with this work, fuel system rig testing of some prototype components will be conducted to evaluate the performance and wear resistance of the cermet material in a potential application in the next-generation fuel system at Cummins.

## Results

The first injection-molded batch was successfully completed. It achieved over 99% density when sintered in a non-overpressure argon atmosphere. The microstructure (see Figure 1) shows the porosity and TiC particles are well distributed throughout the structure. The high-magnification scanning electron microscope (SEM) image in Figure 2 shows good wetting of the TiC particles. This first batch had a higher shrinkage rate than expected; therefore,



**Figure 1.** SEM backscattered image of polished cross-section of injection-molded TiC/Ni<sub>3</sub>Al cermet. The black spots are porosity, the dark gray phase is the TiC, and the light phase is the Ni<sub>3</sub>Al matrix.



**Figure 2.** SEM backscattered image of the sample shown in Figure 1. No delamination between the TiC particles and the Ni<sub>3</sub>Al particles is observed.

a second sintering run was performed after some slight tooling changes to accommodate the new shrinkage rate. This run produced similar results to the first.

The application testing at Cummins Fuel Systems commenced with parts machined from isostatically pressed rods of the TiC/Ni<sub>3</sub>Al material. The application experiences both sliding and impact loading, and 350 hours of abusive testing was conducted between two tests. No observable damage was present on the impact surface, and the sliding wear surface was pristine, as was the mating steel component.

## **Conclusions**

Process optimization work at CoorsTek has progressed well, and CoorsTek is able to create functional test pieces for component evaluation at Cummins. Cummins has shown that the material has a viable application in its next-generation fuel system.

